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# EFFECTIVE CARBON NUMBER OF METHANE IN GAS CHROMATOGRA-PHY

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## SUMMARY

The linearity of the relationship between the logarithm of the corrected retention time and the carbon number of $C_1$–$C_7$ n-alkanes is examined using gas–liquid and gas–solid chromatography. The effective carbon number of methane is shown to be variable but in most instances is substantially closer to unity than the value of 0.5 reported previously.

## INTRODUCTION

The advantage in practice of the retention index schem developed by Kováts[1] relies on the existence of a linear relationship between the carbon number of the n-alkanes and the logarithm of the corrected retention. Both linearity and non-linearity have been reported[2–5] and, as might be expected, these have almost exclusively been concerned with the lower molecular weight homologues as both enhanced[6,7] and reduced retention of these homologues with more polar functional classes frequently occurs particularly on polar stationary phases.

Parcher and Johnson[8] used the retention data of inert gases in order to calculate the dead-time. When the dead-time estimated by this method was used to correct the retention times of n-alkanes it was noted that the retention of methane did not fit on the straight line plot of the logarithm of retention time *versus* carbon number for alkanes up to pentane. From the plots of the logarithm of retention time *versus* carbon number, it was found that methane had a retention time corresponding to an effective carbon number of 0.5. The retention data of the n-alkanes from methane to pentane were used to calculate the dead time ($t_m$) by the iterative technique of Guardino *et al.*[9]. Estimates of $t_m$ were made by assigning carbon numbers of 0, 0.5 and 1 to methane. The values of $t_m$ calculated when methane was assigned a carbon number of 0.5 were similar to those found from the retention times of the inert gases. The values of $t_m$ estimated by assigning carbon numbers of 0 and 1 for methane were less than and greater than, respectively, the retention of the inert gas.

Linearity of the above n-alkane plot has been considered on stationary phases of increasing polar character with calculation of the dead time and with determination of the deviation of the data points from the calculated line[3]. The method

described by Ševčik and Löwentap[10,11] was used as it has been found to allow an accurate calculation of the adjusted retention time by using the ratio, $A$, of the time differences for neightbouring $n$-alkanes in a homologous series. The values for the calculated and experimentally determined retention times of the alkanes on three stationary phases, SE-30, OV-25 and SILAR-7CP, showed excellent agreement, indicating that the $n$-alkane plots are essentially linear. Similarly the plots of corrected retention showed complete linearity even for methane, ethane and propane. However, low values of $A$ were obtained for $C_1$–$C_2$–$C_3$ $n$-alkanes and higher values for $C_2$–$C_3$–$C_4$ $n$-alkanes, indicating some curvatore in the plots for the gaseous species. The method, which considers only differences between experimentally measured points, is more sensitive than other methods and particularly with graphical representation, which is inherently insensitive.

The inconsistencies in the calculated $A$ values were first thought to be due to the fact that the differences in the retention times of these species are small, thereby resulting in an inaccurate measurement. This was not so, however, as the differences for $C_1$–$C_2$–$C_3$ and $C_5$–$C_6$–$C_7$ $n$-alkanes are of the same order. The experimental evidence clearly shows that some minor non-linearity occurs, probably below $C_5$, and the proposal of Parcher and Johnson[8] to use a modified value for the data point showing the greatest deviation, *i.e.*, methane, would be expected to improve the linearity of the $n$-alkane plot.

This work utilizes data obtained by conventional gas–liquid chromatography on dimethyl polysiloxane (SE-30) and on columns involving gas–solid chromatography, *i.e.*, Porapaks, Porasils and squalane on Porasil C, and presents calculated effective carbon numbers for methane on a wider range of stationary phases than were used by Parcher and Johnson[8], and was initated to investigate the use of such a low value (0.5) for methane considering that mathematically the variations from linearity appeared to be so small.

THEORETICAL

If the linear relationships between carbon number of $n$-alkanes and the logarithm of their net retention volume were perfect then retention times would be related to carbon number by

$$\log (t_r - t_m) = bZ + C \tag{1}$$

If the system dead time, $t_m$, is a constant then for the $i$th $n$-alkane eqn. 1 becomes

$$\log (t_{r_i} - t_m) = bZ_i + C \tag{2}$$

Considering three adjacent $n$-alkanes the retention times are related to carbon number by

$$t_{r_n} = t_m + e^{bZ_n} e^c \tag{3a}$$

$$t_{r_{n+1}} = t_m + e^{bZ_{n+1}} e^c \tag{3b}$$

and

$$t_{r_{n+2}} = t_m + e^{bZ_{n+2}} e^c \tag{3c}$$

By subtraction and taking into account that

$$Z_{n+1} = Z_n + 1 \text{ and } Z_{n+2} = Z_n + 2$$

we obtain

$$\Delta t_n = t_{r_{n+1}} - t_{r_n} = e^{b(Z_{n-1})} - e^{b(Z)} e^c = e^{bZ} e^c (e^b - 1) \tag{4a}$$

$$\Delta t_{n+1} = t_{r_{n+2}} - t_{r_{n+1}} = e^{b(Z_{n+2})} - e^{b(Z_{n-1})} e^c = e^{b(Z+1)} e^c (e^b - 1) \tag{4b}$$

$$A = \frac{\Delta t_{n+1}}{\Delta t_n} = \frac{e^{b(Z+1)}}{e^{bZ}} = \frac{e^{bZ} e^b}{e^{bZ}} = e^b \tag{5}$$

$$\log A = \log \left( \frac{t_{r_{n+2}} - t_{r_{n+1}}}{t_{r_{n+1}} - t_{r_n}} \right) = b \tag{6}$$

Thus the slope of the $n$-alkane line can be estimated without direct calculation of the dead-time $t_m$ by eqn. 6 using differences in retention times of three successive $n$-alkanes.

The values of $b$, $c$ and $t_m$ in eqn. 1 were estimated using the procedure of Grobler and Balizs[12].

Constancy of the values of $A$ over the whole of a series of $n$-alkanes is a measure of the linearity of the $n$-alkane line. This has previously been shown to be a rigid test of linearity[4]. In previous papers[4,5] we have in fact shown that the alkane line is non-linear for methane for both non-polar supported liquid phases and porous polymer packings. There is much controversy in the literature concerning the use of the retention time of methane as an estimate of $t_m$. Parcher and Johnson[8] have suggested that if the partition ratios given by

$$k = \frac{t_r - t_m}{t_m} \tag{7}$$

are greater than 3 for all $n$-alkanes used in the mathematical estimation of $t_m$ then the error induced by using methane retention for $t_m$ will be less than 1%. Further, for solutes with $k$ values less than 2, the $t_m$ value determined from methane retention may be grossly in error and mathematical estimation of dead time must be employed.

EXPERIMENTAL

The chromatography was carried out using a Hewlett-Packard 5750 Research Chromatograph interfaced to a 32K PDP11/40 computer. Interfacing was achieved

TABLE I

RETENTION DATA FOR $n$-ALKANES ON SE-30

$Z$ = carbon number of $n$-alkane; $t$ = measured retention time in seconds; $\Delta t$ = measured time between successive $n$-alkanes in seconds; $A$ = difference ratios of Sevcik[9,10]; $t'$ = corrected retention in seconds; $t'$ = $(t - t_m)$ where $t_m$ = dead volume; $Z_{calc}$ = calculated value of carbon number of appropriate $n$-alkane using the equation $Z_{calc} = [\ln(t - t_m) - C]/b$.

| $Z\star$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 200.6 | | | 11.4 | 1.12 |
| | | 12.0 | | | |
| 2 | 212.6 | | 1.75 | 23.4 | 2.11 |
| | | 21.0 | | | |
| 3 | 233.6 | | 2.28 | 44.4 | 2.99 |
| | | 47.9 | | | |
| 4 | 281.5 | | 2.05 | 92.3 | 4.00 |
| | | 98.4 | | | |
| 5 | 379.9 | | 2.06 | 190.7 | 5.00 |
| | | 203.0 | | | |
| 6 | 582.9 | | 2.06 | 393.7 | 6.00 |
| | | 420.1 | | | |
| 7 | 1003.0 | | | 813.8 | 7.00 |
| | | | $\bar{A}$ = 2.06 | | |

$\star$ Based on $Z$ = 4–7: $t_m$ = 189.2 sec; $b$ = 0.726; $c$ = 1.62.

TABLE II

RETENTION DATA FOR $n$-ALKANES ON PORASIL C

| $Z\star$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 158.5 | | | 17.1 | 0.92 |
| | | 24 | | | |
| 2 | 182.5 | | 1.94 | 41.1 | 2.03 |
| | | 26.5 | | | |
| 3 | 229 | | 2.29 | 87.6 | 2.99 |
| | | 106.3 | | | |
| 4 | 335.3 | | 2.20 | 193.9 | 4.00 |
| | | 232.7 | | | |
| 5 | 568 | | 2.20 | 426.6 | 5.00 |
| | | 511 | | | |
| 6 | 1079 | | 2.20 | 937.6 | 6.00 |
| | | 1127 | | | |
| 7 | 2206 | | | 2064.6 | 7.00 |
| | | | $\bar{A}$ = 2.20 | | |

$\star$ Based on $Z$ = 4–7: $t_m$ = 141.4 sec; $b$ = 0.789; $c$ = 2.11.

TABLE III

RETENTION DATA FOR $n$-ALKANES ON SQUALANE ON PORASIL C

| $Z\star$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 136 | | | 26.3 | 1.31 |
| | | 28.5 | | | |
| 2 | 164.5 | | 2.04 | 54.8 | 2.17 |
| | | 58.0 | | | |
| 3 | 222.5 | | 2.60 | 112.8 | 3.01 |
| | | 150.5 | | | |
| 4 | 373 | | 2.37 | 263.3 | 4.00 |
| | | 357 | | | |
| 5 | 730 | | 2.37 | 620.3 | 5.00 |
| | | 846.5 | | | |
| 6 | 1576.5 | | 2.34 | 1466.8 | 6.00 |
| | | 1980 | | | |
| 7 | 3556.5 | | | 3446.8 | 7.00 |
| | | | $\bar{A}$ = 2.36 | | |

$\star$ Based on $Z$ = 4–7: $t_m$ = 109.7 sec; $b$ = 0.857; $c$ = 2.15.

TABLE IV

RETENTION DATA FOR n-ALKANES ON PORAPAK S

| $Z\star$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 58.5 | 13.8 | | 14.2 | 1.05 |
| 2 | 72.3 | 22.0 | 1.59 | 28.0 | 2.10 |
| 3 | 94.3 | 45.2 | 2.06 | 50.0 | 3.00 |
| 4 | 139.5 | 86.3 | 1.91 | 95.2 | 4.00 |
| 5 | 225.8 | 164.0 | 1.90 | 181.5 | 5.00 |
| 6 | 389.8 | 313.5 | 1.91 | 345.5 | 6.00 |
| 7 | 703.3 | | 1.91 | 659.0 | 7.00 |
| | | | $\bar{A} = 1.91$ | | |

★ Based on $Z = 4$–$7$: $t_m = 44.3$ sec; $b = 0.645$; $c = 1.98$.

TABLE V

RETENTION DATA FOR n-ALKANES ON PORAPAK PS

| $Z\star$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 61.5 | 11.0 | | 12.5 | 1.37 |
| 2 | 72.5 | 21.5 | 1.95 | 23.5 | 2.18 |
| 3 | 94 | 53.0 | 2.47 | 45.0 | 3.01 |
| 4 | 147 | 116.8 | 2.20 | 98.0 | 4.00 |
| 5 | 263.8 | 255.7 | 2.19 | 214.8 | 5.00 |
| 6 | 519.5 | 560.8 | 2.19 | 470.5 | 6.00 |
| 7 | 1080.3 | | 2.19 | 1931.3 | 7.00 |
| | | | $\bar{A} = 2.20$ | | |

★ Based on $Z = 4$–$7$; $t_m = 49.0$ sec; $b = 0.784$; $c = 1.45$.

TABLE VI

RETENTION DATA FOR n-ALKANES ON PORAPAK Q

| $Z\star$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 71.5 | 19.0 | | 16.1 | 0.67 |
| 2 | 90.5 | 27.0 | 1.41 | 35.1 | 2.00 |
| 3 | 117.5 | 50.8 | 1.88 | 62.1 | 2.98 |
| 4 | 168.3 | 89.7 | 1.77 | 112.9 | 4.00 |
| 5 | 258.0 | 161.0 | 1.79 | 202.6 | 5.00 |
| 6 | 419.0 | 288.9 | 1.79 | 363.4 | 6.00 |
| 7 | 707.9 | | 1.79 | 652.5 | 7.00 |
| | | | $\bar{A} = 1.73$ | | |

★ Based on $Z = 4$–$7$: $t_m = 55.4$ sec; $b = 0.584$; $c = 2.39$.

TABLE VII

RETENTION DATA FOR n-ALKANES ON PORAPAK R

| $Z^*$ | $t$ | $\Delta t$ | $A$ | $t'$ | $Z_{calc}$ |
|---|---|---|---|---|---|
| 1 | 44.5 | 10.8 | | 9.1 | 0.87 |
| 2 | 55.3 | 15.7 | 1.45 | 19.9 | 2.10 |
| 3 | 71.0 | 31.5 | 2.01 | 35.6 | 3.01 |
| 4 | 102.5 | 60.0 | 1.90 | 67.1 | 4.00 |
| 5 | 162.5 | 113.3 | 1.89 | 127.1 | 5.00 |
| 6 | 275.8 | 215.2 | 1.90 | 240.4 | 6.00 |
| 7 | 491.0 | | | 455.6 | 7.00 |
| | | | $\bar{A} = 1.83$ | | |

* Based on $Z = 4$–7: $t_m = 35.4$ sec; $b = 0.63$; $c = 1.65$.

by the use of an LPS 11 Laboratory Periperhal System consiting of a 12-bit analogue-to-digital converter, a programmable real-time clock with two Schmitt triggers and a digital controller with two 12-bit digital-to-analogue converters. Injection was effected using a Hewlett-Packard 7670 A automatic sampler.

The columns used and their operating temperatures were as follows:

(1) 22 ft. × 0.25 in. O.D. aluminium packed with 10% SE-30 on Chromosorb W AW DMCS, operated at 30°C.

(2) 6 ft. × 0.125 in. O.D. PTFE column packing packed with Porasil C (75–125 μm), operated at 60°C.

(3) 10 ft. × 0.125 in. O.D. PTFE packed with 10% squalane on Porasil C, operated at 50°C.

TABLE VIII

CALCULATED CARBON NUMBERS FOR $C_1$ $C_3$ AND PARTITION RATIOS FOR $C_4$–$C_7$ n-ALKANES

| Parameter | Z | SE-30 | Porasil C | Squalane on Porasil C | Porapak S | Porapak PS | Porapak Q | Porapak R |
|---|---|---|---|---|---|---|---|---|
| Calculated carbon | 1 | 1.12 | 0.92 | 1.31 | 1.05 | 1.37 | 0.67 | 0.87 |
| number values for | 2 | 2.11 | 2.03 | 2.17 | 2.10 | 2.18 | 2.00 | 2.10 |
| methane, ethane and | 3 | 3.99 | 2.99 | 3.01 | 3.00 | 3.01 | 2.98 | 3.01 |
| propane on the stationary phases indicated* | | | | | | | | |
| Partition ratios** of | 4 | 0.49 | 1.37 | 2.40 | 2.15 | 2.00 | 2.04 | 1.89 |
| $C_4$–$C_7$ n-alkanes used | 5 | 1.01 | 3.02 | 5.66 | 4.10 | 4.39 | 3.66 | 3.89 |
| in calculating $t_m$ | 6 | 2.08 | 6.63 | 13.38 | 7.80 | 9.61 | 6.56 | 6.79 |
| | 7 | 4.30 | 14.60 | 31.43 | 14.87 | 21.07 | 11.77 | 12.86 |

* Calculated carbon numbers for $C_4$–$C_7$ n-alkanes were equal to actual carbon numbers to 3 decimal places.

** Calculated by $k = t'/t_m$ (ref. 8).

(4) Each 6 ft. × 0.125 in. O.D. PTFE packed with (4) Porapak S (80–100 $\mu$m), operated at 180°C, (5) Porapak PS (80–100 $\mu$m), operated at 110°C, (6) Porapak Q (80–100 $\mu$m), operated at 220°C and (7) Porapak R (80–100 $\mu$m), operated at 180°C.

## RESULTS AND DISCUSSION

The results obtained on the various columns are presented in Tables I–VIII. The $A$ values on all of the columns are significantly different for the $C_1$–$C_2$ alkanes compared with the $C_2$–$C_3$ alkanes, which vary slightly for the values of all of the other alkane pairs which are essentially constant. These values further show that some non-linearity occurs with the $n$-alkane plots, particularly with with the $C_1$ and $C_2$ compounds. On this basis, the proposition of Johnson and Parcher[8] that improved linearity will be achieved on modification of the most variant data point is valid. Calculation of values of the carbon numbers on all of the stationary phases according to the equation shown are assembled in Table VIII and for methane over a range of stationary phases the values are variable but in all instances are substantially closer to unity than the 0.5 reported to be a general value by Parcher and Johnson[8]. Table VIII further shows a deviation from unity for the carbon numbers appropriate to ethane but here the values are reduced compared with those of methane, indicating that the original deviation is significantly localized with the methane data point. The calculated carbon numbers for the other alkanes are essentially the theoretical values, indicating, as suggested by the $A$ values, that the plots are linear in these regions.

Also included in Table VIII are the partition ratios calculated for the $C_4$–$C_7$ $n$-alkanes that were used in estimating $t_m$. It is apparent that there is no correlation of the calculated carbon number for methane with the range of $k$ values for the $n$-alkanes as might be expected from the discussion by Parcher and Johnson[8]. The results therefore indicate that, for a wide number of stationary phases, the use of methane retention as an estimate of $t_m$ should be treated with caution. Further, the effective carbon number for methane is not generally $ca.$ 0.5 as previously reported[8].

## REFERENCES

1  E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
2  H. Groenendijk and A. W. C. van Kemenade, *Chromatographia*, 1 (1968) 472.
3  L. Rohrschneider, *Chromatographia*, 2 (1969) 437.
4  M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 188 (1980) 246.
5  M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 198 (1980) 156.
6  J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 101 (1974) 103.
7  J. K. Haken, D. K. M. Ho and M. S. Wainwright, *J. Chromatogr.*, 106 (1975) 327.
8  J. F. Parcher and D. M. Johnson, *J. Chromatogr. Sci.*, 18 (1980) 267.
9  X. Guardino, J. Albaigés, G. Firpo, R. Rodríguez-Viñals and M. Gassiot, *J. Chromatogr.*, 118 (1976) 13.
10 J. Ševčik, *J. Chromatogr.*, 135 (1977) 183.
11 J. Ševčik and M. S. H. Löwentap, *J. Chromatogr.*, 147 (1978) 75.
12 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.